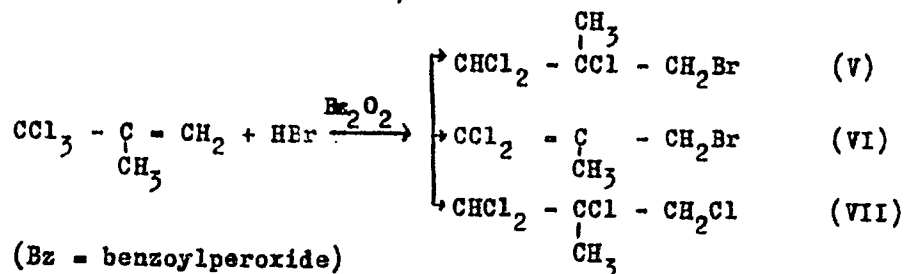


Hetero- and Homolytical Rearrangements in the Chemical SOV/62-59-6-12/36
Transformation of 1,1,1-Trichloro-2-methylpropene

diction to Markovnikov's rule. When heated, the affiliation yielded the following products (the formation scheme is still more in detail dealt with):



The substances produced were identified by determining their melting point. 1,1,1-Trichloro-2-methylpropene reacts with benzene, toluene, and nucleophilic reagents with an allyl rearrangement. In the experimental part the different reactions are described in detail. There are 6 references, 5 of which are Soviet.

Card 2/3

Hetero- and Homolytical Rearrangements in the Chemical SOV/62-59-6-12/36
Transformation of 1,1,1-Trichloro-2-methylpropene

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR
(Institute of Elemental Organic Compounds of the Academy of
Sciences, USSR)

SUBMITTED: September 30, 1957

Card 3/3

5 (3)

AUTHORS:

Nesmeyanov, A. N., Borisov, A. Ye., SOV/62-59-6-13/36
Savel'yeva, I. S.

TITLE:

Addition of Triethyl Aluminum to Tolan (Prisoyedeneniye trietilal'yuminiya k tolanu)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 6, pp 1034 - 1036 (USSR)

ABSTRACT:

For the purpose of the addition reaction mentioned in the title, equimolecular quantities of triethyl aluminum and of 1,2-diphenylacetylene were together heated up to 100-120°. Both substances formed the liquid 1,2-diphenylbuten (I) with a boiling point of 108-109°, $n_D^{20} = 1.5965$, yield 40% - and crystalline 1,2,3,4-tetraphenyl butadien-1,3 (II) which melts at 90-91° and at 129-130° (Two stereoisomers). Separation of both substances could be carried out either chromatographically or by crystallisation. The configuration of both substances was determined by plotting the infrared spectra of each isomer and interpreting them. Characteristic bands were found for the liquid and solid isomer of (I), according to which the liquid

Card 1/2

Addition of Triethyl Aluminum to Tolan

SOV/62-59-6-13/36

isomer has a cis- and the solid one a transconfiguration. The three possible isomers of (II) could not be determined by means of the infrared spectrum. In the experimental part the different reactions are described in detail, and in a table the yields in reaction products are compiled. There are 1 table and 4 references, 1 of which is Soviet.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR
(Institute of Elemental Organic Compounds of the Academy of Sciences, USSR)

SUBMITTED: October 24, 1957

Card 2/2

5 (3)

AUTHORS:

Nesmeyanov, A. N., Borisov, A. Ye.,
~~Novikova, N. V.~~

SOV/62-59-7-10/38

TITLE:

Preservation of the Configuration of the Radical in the Metal
Exchanging Reactions of Propenyl Metal Organic Compounds
(Sokhraneniye konfiguratsii radikala v reaktsiyakh obmena
metalla propenil'nykh metalloorganicheskikh soyedineniy)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
1959, Nr 7, pp 1216-1224 (USSR)

ABSTRACT:

This paper belongs to a series of investigations on the stereo-
chemical exchange of atoms bound to olefin carbon. The relative
scheme shows that the cis- or transconfiguration of the olefin
radical remains preserved in an electrophilic or homolytic
substitution. As initial materials for the investigations cis-
and trans-1-bromopropene were used. The lithium salts of these
compounds were subjected to a metal exchange. Lithium was
replaced by mercury, thallium or tin. The configuration of the
stereoisomeric lithium propenyl was determined by means of the
infrared absorption spectrum and the configuration of the Hg-,
Tl- and Sn-compounds was determined by means of the infrared
spectrum and according to the method of even and uneven numbers

Card 1/2

Preservation of the Configuration of the Radical in the SOV/62-59-7-10/38
Metal Exchanging Reactions of Propenyl Metal Organic Compounds

of links in the cycles. The investigation of the metal exchange was carried out at room temperature. The metals were exchanged in an electrophilic reaction. A reaction hitherto unknown was noticed: $R_2SnCl_2 + TlCl_2 \longrightarrow R_2TlCl_2 + SnCl_4$. In the experimental part the various exchange reactions are described. There are 7 references, 2 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR
(Institute of Elemental Organic Compounds of the Academy of Sciences, USSR)

SUBMITTED: November 12, 1957

Card 2/2

5 (4)

AUTHORS:

Nesmeyanov, A. N., Nogina, O. V.,
Dubovitskiy, V. A.

SOV/62-59-8-32/42

TITLE:

Effect of the Time Factor on the Degree of Association of
Titanium Alkoxy Derivatives in a Benzene Solution

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
1959, Nr 8, pp 1496-1498 (USSR)

ABSTRACT:

This brief survey discusses the property dealt with in numerous
papers (Refs 1-3) of the alkoxy derivatives of titanium to
associate in aqueous benzene solutions. It has been shown that
the methods used for the determination of the molecular weight
(kryoscopy and ebullioscopy) yielded a higher molecular weight
than corresponded to the monomer. The authors of the present
paper now succeeded in showing that the degree of association of

the substances: $(RO)_4Ti$, $ClTi(OR)_3$, $(RO)_2TiO$, $\begin{matrix} Cl \\ \diagup \\ TiO, \\ \diagdown \\ RO \end{matrix}$, $\begin{matrix} Cl \\ \diagup \\ TiO \cdot ROH, \\ \diagdown \\ RO \end{matrix}$

$Cl_2TiO \cdot 2ROH$ changes gradually. It diminishes and, after some

hours, equals 1. The decomposition rate of the associates,
however, is not high, while the activation energy of the

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Effect of the Time Factor on the Degree of Association of Titanium Alkoxy Derivatives in a Benzene Solution SOV/62-59-8-32/42

dissociation of the associates is considerable. Figures 1 and 2 show the change in molecular weight of some of the relevant substances in the course of time. The table contains the molecular weights of the substances under investigation. Some substances had been synthesized by the authors for the purposes of this paper and had actually been obtained for the first time. It was seen from the curves that initial monomers are formed by dissociation. Thus it is possible to use kryoscopy for the determination of the molecular weights of the compounds under investigation. The authors will report on the newly synthesized substances in future papers. There are 3 figures, 1 table, and 5 references, 1 of which is Soviet.

ASSOCIATION: Institut elementorganicheskikh soyedineniy Akademii nauk SSSR
(Institute of Elemental-organic Compounds of the Academy of Sciences, USSR)

SUBMITTED: February 18, 1959

Card 2/2

ELSMETANOV, A.N.

Promote the role of our people in the management of scientific
research. NFO no.10:10-12 O '59. (MIRA 13:2)

1. Prezident AN SSSR.
(Research, Industrial)

5.3600

77065
SOV/62-59-12-9/43

AUTHORS: Nesmeyanov, A. N., Semenov, N. A.

TITLE: Preparation of α, α, ω -Trichloroalkenes From $\alpha, \alpha, \alpha, \omega$ -Tetrachloroalkanes

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk. 1959, Nr 12, pp 2119-2121 (USSR)

ABSTRACT: Some higher $\alpha, \alpha, \alpha, \omega$ -tetrachloroalkanes, obtained by telomerization of ethylene with carbon tetrachloride, were dehydrochlorinated over $ZnCl_2$, at 135-150°, for 3 hr to form $CCl_2=CH(CH_2)_9Cl$ (yield 74%; bp 122-123° at 2mm, n_D^{20} 1.4820) and $CCl_2=CH(CH_2)_{11}Cl$ (yield 70%; bp 147-148° at 2 mm, n_D^{20} 1.4805). 1,1,1,3-Tetrachloropropane was similarly dehydrochlorinated to 1,1,3-trichloroprop-1-ene (yield 76%; bp 132-132.5°, n_D^{20} 1.4948). The same reaction can be accomplished in 53% yield by using KOH in

Card 1/2

Preparation of α, α, ω -Trichloroalkenes
From $\alpha, \alpha, \alpha, \omega$ -Tetrachloroalkanes

77065
SOV/62-59-12-9/43

ethylcellosolve. There are 4 references, 3 Soviet,
1 U.K. The U.K. reference is: British patent 581901
and 2410541.

ASSOCIATION: Institute of Element-Organic Compounds, Academy of
Sciences, USSR (Institut elementoorganicheskikh
soyedineniy Akademii Nauk SSR)

SUBMITTED: April 14, 1958

Card 2/2

77066
50V/62-59-12-10/43

Kost, V. N., Sidorova, Z. Z., Freydlina, R. Kh.,
Nesmeyanov, A. N.

Synthesis of α -Chloro-carboxylic Acids by Addition of Chlorine in Formic Acid to Compounds Containing the $Cl_2C=CH$ -Group

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 12, pp 2122-2125 (USSR)

The reaction

$$x \text{ CH}_3\text{CH}=\text{CH}_2 + \text{Cl}_2 \xrightarrow{\text{KOH}} x (\text{CH}_3)_2\text{C}(\text{COOCH})_2 + x \text{HCl}$$

is conducted by gradually passing chlorine through a solution of appropriate crotonolefin at 30°C. The following acids were prepared in this manner: crotonic acid from crotonolefin; 3-formylcrotonic acid, yield 73%, mp 66-67° (from benzene); 3-chloro-8-termaoxalvaleric acid, yield

Card 1/2

82%, bp 138° (1.5 mm), n_D^{20} 1.4671; **3**, δ -dichlorovaleric acid, α , ω -dichloroacetic acid; and **4**, ω -dichloro-nonoic acid, yield 71%, bp 142-143° (0.5 mm), n_D^{20} 1.4768. There are 8 Soviet references.

ASSOCIATION: Institute of Element-Organic Compounds, Academy of Sciences, USSR (Institut elementoorganicheskikh soedineniy Akademii nauk SSSR)

SUBMITTED: March 25, 1958

Card 2/2

NESMEYANOV, A.N.; TSIFKA, I.

Chemical state of atoms produced by nuclear transformations.

Part 3. Radiokhimiia 1 no.1:82-85 '59.

(MIRA 12:4)

(Phosphorus--Isotopes)

NESMEYANOV, A.N.; BORISOV, Ye.A.

Chemical action of radioactive bromine atoms produced by the
reaction of bromine with neutrons in chlorobromomethane, dichloro-
bromomethane, and chlorodibromomethane. Radiokhimiya 1 no.1:86-90
'59. (MIRA 12:4)

(Bromine—Isotopes) (Neutrons) (Methane)

NESMAYANOV, A.N.; SAZONOV, L.A.

~~Measurement of the saturated vapor pressure of lithium chloride.~~
Zhur.neorg.khim. 4 no.1:231-233 Ja '59. (MIRA 12:2)
(Lanthanum chlorides) (Vapor pressure)

5(2)

AUTHORS:

~~Nesmeyanov, A. N.~~, Anisimov, K. N., Mikheyev, Ye. P.,
Volkov, V. L., Valuyeva, Z. P.

SOV/78-4-2-1/40

TITLE:

Preparation of Tungsten Carbonyl by the Interaction of
Iron Pentacarbonyl With Tungsten Hexachloride (Polucheniye
karbonila vol'frama vzaimodeystviyem pentakarbonila zheleza
s shestikhloristym vol'framom)

PERIODICAL:

Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 2,
pp 249-252 (USSR)

ABSTRACT:

The interaction of tungsten-6-chloride with iron pentacarbonyl
in an ethyl ether medium was investigated. The tests in the
autoclave were carried out at the following molar ratios of
the individual components: $WCl_6 : Fe(CO)_5 = 1 : 2.25$ and
 $1 : 3.25$. The temperatures during the tests were: 70, 90, 110,
130, 150, 170 and 190°. At the molar ratio $Fe(CO)_5 : WCl_6 =$
 $= 3.25 : 1$ the yield of $W(CO)_6$ increases with temperature;
it shows an increase of 29-31% at 20°, of 36-42% at 70°, and
of 72-75% at 90°. The course of the reaction is shown in the

Card 1/2

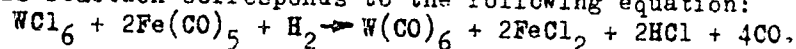
SOV/78-4-2-1/40

Preparation of Tungsten Carbonyl by the Interaction of Iron Pentacarbonyl
With Tungsten Hexachloride

following equation: $WCl_6 + 3Fe(CO)_5 \rightarrow W(CO)_6 + 3FeCl_2 + 9CO$.

The supply of hydrogen to the reaction mixture, after the conclusion of the reaction, increases the $W(CO)_6$ yield to

85%. This reaction corresponds to the following equation:



The production of tungsten hexacarbonyl is described in detail. Results which are well reproducible are obtained by this method. There are 2 tables and 7 references, 3 of which are Soviet.

SUBMITTED: December 9, 1957

Card 2/2

NESMEYANOV, A.N.; IOFA, B.Z.

Saturated vapor pressure of solid lead fluoride. Zhur.neorg.khim. 4
no.2:486-488 F '59. (MIRA 12:3)
(Lead fluoride) (Vapor pressure)

5(2)

SOV/78-4-3-2/34

AUTHORS: ~~Naumoyanov, A. N.~~, Mikheyev, Ye. P., Anisimov, K. N.,
Volkov, V. L., Valuyeva, Z. P.

TITLE: The Synthesis of Molybdenum Carbonyl by Interaction Between
Iron Pentacarbonyl and Molybdenum Pentachloride (Sintez
karbonila molibdena vzaimodeystviyem pentakarbonila zheleza s
pyatikhloristym molibdenom)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 3,
pp 503-505 (USSR)

ABSTRACT: It has been found that molybdenum hexacarbonyl is formed in a
maximum yield of 28.5% by the interaction between iron penta-
carbonyl and molybdenum pentachloride in the presence of
hydrogen chloride under a carbon monoxide pressure in an ether
medium. Molybdenum hexacarbonyl is formed in a 15% yield at
175° in the presence of compressed hydrogen in an ethyl ether
medium. Molybdenum carbonyl is formed in a yield of 23.4% at
175° when the reaction is performed in an autoclave with
hydrogen (initial pressure 100 atmospheres) and carbon monoxide
(initial pressure 50 atmospheres). There are 2 tables and
1 Soviet reference.

Card. 1/2

SOV/78-4-3-2/34

The Synthesis of Molybdenum Carbonyl by Interaction Between Iron Pentacarbonyl and Molybdenum Pentachloride

SUBMITTED: December 24, 1957

Card 2/2

NESMEYANOV, A.N., professor

Ways and means of stabilizing radioactive atoms produced as a
result of nuclear transformations. Khim.nauka i prom. 4 no.4:
435-441 '59. (MIRA 13:8)

(Radioisotopes)

(Nuclear reactions)

5(2)

AUTHORS:

SOV/78-4-8-19/43

Nesmeyanov, R. N., Anisimov, K. N., Volkov, V. L.,
Fridenberg, A. E., Mikheyev, Ye. P., Medvedeva, A. V.

TITLE:

The Synthesis of Chromium Hexacarbonyl by the Reaction of Chromium Trichloride With Lithium Aluminum Hydride and Carbon Oxide Under Pressure (Sintez geksakarbonila khroma vzaimodeystviyem trekhkhlorigo khroma s litilyuminiygidridom i okis'yu ugleroda pod davleniyem)

PERIODICAL:

Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 8, pp 1827-1828 (USSR)

ABSTRACT:

If the reaction mentioned in the title is carried out at a ratio of 1 mole CrCl_3 : 3 mole LiAlH_4 in etheric solution at 65°C and a pressure of 100 at, $\text{Cr}(\text{CO})_6$ is obtained in a 65% yield. The hitherto published data (Refs 1-6) show lower yields. A lower content of lithium aluminum hydride in the reaction mixture and lower temperatures strongly reduce the yields (Table 1). There are 1 table and 7 references, 3 of which are Soviet.

Card 1/2

5(2)

SOV/78-4-9-3/44

AUTHORS: Nesmeyanov, A. N., Mikheyev, Ye. P., Anisimov, K. N.,
Filimonova, N. P.

TITLE: The Synthesis of the Chromium Hexacarbonyl With Participation
of Metallic Reducing Agents

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 9,
pp 1958-1960 (USSR)

ABSTRACT: Reference is made to the studies on $\text{Cr}(\text{CO})_6$ described in
publications (Refs 1-5, 7, 8). The difficulty encountered
in synthesizing this substance lies in the high electrode
potential of chromium trichloride, as this makes the use
of strongly reducing metals necessary, which simultaneously
give side reactions with the solvent. The only comparatively
indifferent solvent was stated to be pyridine, which does
not react with the alkali metals and forms complex compounds
with $\text{Cr}(\text{CO})_6$. CrCl_3 was dissolved in pyridine and reacted with
CO under higher pressure after addition of zinc powder at
175° and yielded 10.8% $\text{Cr}(\text{CO})_6$. The authors obtained a 35%
yield of the same substance, by applying 50% excess magnesium
activated by a crystal of iodine. Without activation by iodine
the yield sank to 4%, as the magnesium did not react. An

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SOV/78-4-9-3/44

The Synthesis of the Chromium Hexacarbonyl With Participation of Metallic Reducing Agents

increase in the CO pressure to 220 atm also passivated the magnesium (only 1.7% yield). Appreciable yields were obtained with sodium (150% theoretical amount) at 20-25°. Raising the temperature to 50° lowered the yield. However, a rise in pressure to 220 atm increased the yield to 37%. The same yield was obtained by using lithium instead at a pressure of only 70 atm, but a further rise in the CO pressure had no effect on the yield. There are 9 references, 2 of which are Soviet.

SUBMITTED: May 28, 1958

Card 2/2

5(3)

SOV/79-29-9-2/76

AUTHORS:

Nesmeyanov, A. N., Lutsenko, I. F., Khomutov, R. M., Dubovitskiy, V. A.

TITLE:

Vinyl Esters of Sulfonic Acids

PERIODICAL:

Zhurnal obshchey khimii, 1959, Vol 29, Nr 9,
pp 2817 - 2820 (USSR)

ABSTRACT:

To synthesize the vinyl esters of various carboxylic acids the authors made use of the reaction of acid halides of carboxylic acids with halogen mercury acetaldehyde or halogeno mercury ketones, the only reaction products being the acetates of the enol forms of oxo compounds (Refs 1,2). The said reaction did not always exhibit the same character: thus, for example, the chloro carbonic acid ester, the acid chlorides of sulfonic acids, and silicon tetrachloride did not react with the halogeno mercury oxo compounds. Mercury bisacetaldehyde $\text{Hg}(\text{CH}_2\text{CHO})_2$ (Ref 3) synthesized by the authors, proved to be more reactive as compared with the above aldehyde: this permitted the acid chlorides of the sulfonic acids to be introduced into the reaction according to the following

Card 1/3

Vinyl Esters of Sulfonic Acids

SO7/79-29-9-2/76

scheme:



Chloro mercury acetaldehyde did not react any more. Mercury bisketones reacted in the same manner. To prevent the vinyl ester of sulfonic acid from polymerizing, pyridine must be added, and the mercury salts must be removed from the reaction solution. By complying with these prudential measures, the vinyl esters of methane- and ethane sulfonic acid were obtained in yields of 45 or 47%. The yields of vinyl esters of benzene- and p-toluene sulfonic acid amounted to 70 and 75% correspondingly. Reaction of thionyl chloride with mercury bisacetaldehyde yielded divinyl sulfite (45%); when applying sulfuryl chloride it cleaved and developed SO_2 , without any resulting divinyl sulfate. Reaction of vinyl ester of benzene sulfonic acid with benzoyl chloride according to A. Sieglitz and O. Horn (Ref 4) gave a high yield of β, β -dichloropropiophenone according to the suggested scheme 2. The inter-

Card 2/3

Vinyl Esters of Sulfonic Acids

SOV/79-29-9-2/76

mediate product α -chloro- β -benzoyl ethyl-p-toluene sulfonate separated by this reaction was completely transferred into β, β -dichloro propiophenone with the equivalent amount $AlCl_3$; this confirms the above reaction course. There are 4 references, 3 of which are Soviet.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet (Moscow State University)

SUBMITTED: January 8, 1959

Card 3/3

NESMEYANOV, A.N.; SMAGHTIN, L.A.; CHOPOROV, D.Ya.; LEBEDEV, V.I.

Investigation of the thermodynamics of solid solutions of gold
with silver and copper. Part 1 [with summary in English]. Zhur.
fiz.khim. 33 no.2:342-348 F '59. (MIRA 12:4)

1. Moskovskiy gosudarstvennyy universitet im. M.V. Lomonosova.
(Gold-silver alloys) (Gold-copper alloys)
(Vapor pressure)

NESEMAYANOV, A.M., akademik; TOPCHIEV, A.V., akademik; ARTSIMOVICH, L.A.,
akademik

Congratulations to Academician Vasilii Grigor'evich Fesenkov
(on the occasion of his 70th birthday). Astron.zhur. 36 no.1:3
Ja-F '59. (MIRA 12:4)

1. Prezident AN SSSR (for Nesemayanov). 2. Glavnyy uchenyy
sekretar' Prezidiuma AN SSSR (for Topchiyev). 3. Ispolnyayu-
shchiy obyazannosti akademika-sekretarya Otdeleniya fiz.-mat.
nauk AN SSSR (for Artsimovich).

(Fesenkov, Vasilii Grigor'evich, 1889-)

5.3700

77090
SOV/62-59-12-34/43

AUTHORS: Nesmeyanov, A. N., Makarova, L. G.

TITLE: Formation of Organomagnesium Compounds During the
Decomposition of Aryldiazonium Borofluorides With
Magnesium

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh
nauk, 1959, Vol 59, Nr 12, pp 2241-2244 (USSR)

ABSTRACT: Decomposition of aryldiazonium borofluorides with
metallic magnesium in tetrahydrofuran, as well as
in other ethers; or in dimethylformamide yields
organomagnesium compounds. The experiments are
summarized in Table 1.

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TABLE 1. DECOMPOSITION OF ARYLONAZONIUM BORO-
FLUORIDES WITH MAGNESIUM FILINGS IN TETRAHYDR FURAN

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SOV/62-59-12-34/43

NR	A+ N ₂ BF ₄		AMOUNT		REACTION CONDITIONS	REACTION TIME	OBTAINED A-COOH	
	Ar	AMOUNT, in g	Mg, in g	SOLVENT, in ml			in g	m.p.
1	<i>o</i> -CH ₃ C ₆ H ₄	50	5	250	STARTING TEMP, -8°. THE TEMP DID NOT RISE. AFTER 1 MONTH, THE REACTION MIXTURE WAS PERIODICALLY HEATED TO 30°	2 MONTHS AND 10 DAYS	>0.01	104
2	<i>p</i> -CH ₃ C ₆ H ₄	50	5.5	250	TEMP, 2°. TEMP DID NOT RISE	2 MONTHS	>0.01	179
3	<i>p</i> -CH ₃ C ₆ H ₄	50	6	250	STARTING TEMP, -10°; max, -8°	6 DAYS	>0.01	181
4	<i>p</i> -C ₂ H ₅ OC ₆ H ₄	10	0.97	75	STARTING TEMP, -8°; max, 8°	3 DAYS	>0.01	193
5	<i>o</i> -C ₁₀ H ₇	58	5.7	250	STARTING TEMP 22°; max, 32°	2 MONTHS	0.01	159

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Formation of Organomagnesium Compounds
During the Decomposition of Aryldiazonium
Borofluorides With Magnesium

77090
SOV/62-59-12-34/43

There are 2 tables; and 8 references, 6 Soviet,
2 U.S. The U.S. references are: Dunker, M. F.
B., et al., J. Am. Chem. Soc., 58, 2308 (1936); Doak,
G. O., Freedman, L. D., J. Am. Chem. Soc., 73, 5658,
5656 (1951), and 74, 830 (1952).

ASSOCIATION: Institute of the Elementoorganic Compounds of the
Academy of Sciences of the USSR (Institute elemento-
organicheskikh soyedineniy Akademii nauk SSSR)

SUBMITTED: May 5, 1959

Card 3/3

5(3)

AUTHORS:

Nesmeyanov, A. N., Perevalova, E. G.,
Shilovtseva, L. S., Ustynyuk, Yu. A.

SOV/20-124-2-25/71

TITLE:

Synthesis of Ferrocene Derivatives by Means of the
N,N-Dimethyl-Aminomethyl Ferrocene Methiodide (Sintez
proizvodnykh ferrotsena s pomoshch'yu yodmetilata
N,N-dimetilaminometilferrotsena)

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 124, Nr 2, pp 331-334
(USSR)

ABSTRACT:

The compound last mentioned in the title was earlier used by
the authors (Ref 5) for the synthesis of methyl ferrocene. It
proved to be a suitable reagent for the introduction of the
ferrocenyl-methyl group (Refs 2-8). In the present paper some
substitution reactions of the dimethyl-amino group were carried
out, furthermore ~~methyl-ferrocene~~ was aminomethylated and
ferrocene aminoethylated. It was thus possible to obtain the
sodium salt of ferrocenyl-methane sulfonic acid by the interaction
between the compound mentioned in the title and sodium sulfite.
By the influence of potassium thiocyanate ferrocenyl-methyl
thiocyanate was formed. Sodium phenolate and β -naphtholate
yielded the phenyl- and β naphthyl ether of the ferrocene carbinol.

Card 1/3

Synthesis of Ferrocene Derivatives

SOV/20-124-2-25/71

by Means of the N,N-Dimethyl-Aminomethyl Ferrocene Methiodide

By ferrocenyl methylation of the p-oxy-azo benzene an azo compound was formed containing a ferrocenyl group. This had hitherto not been possible. On the aminomethylation of the methyl ferrocene (Ref 5) with a mixture of N,N,N',N'-tetramethyldiamino methane and paraform a homoannular (N,N, dimethyl-amino methyl) methyl ferrocene was obtained in a 60% yield. The aminomethylation of the methyl ferrocene was carried out in the substituted cyclopentadiene ring in a yield which was somewhat higher than for ferrocene (51%, Ref 2). The addition of phosphoric acid increased the yield up to 80%. Besides, diaminomethylated methyl ferrocene is formed (10% yield). Thus the methyl group in the methyl ferrocene considerably activates the ferrocene nucleus against electrophilic attacks. The formation of the homoannular compound suggests that the ring to which the methyl group is bound, is activated to a more considerable degree. The successful production of the diaminomethylated methyl ferrocene further proves that the influence exerted by the substituents is transferred from one cyclopentadienyl ring to the other one by means of the iron atom (Ref 9). From the compound mentioned in the title the authors

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Synthesis of Ferrocene Derivatives

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by Means of the N,N-Dimethyl-Aminomethyl Ferrocene Methiodide

synthesized the homoannular dimethyl ferrocene. It may be assumed from the comparison of infrared spectra that the alkyl groups are in a 1,3-position. There are 12 references, 2 of which are Soviet.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova
(Moscow State University imeni M. V. Lomonosov)

SUBMITTED: October 14, 1958

Card 3/3

5(2,3)

AUTHORS:

Nesmeyanov, A. N., Academician
Lutsenko, I. F., Ponomarev, S. V.

SOV/20-124-5-31/62

TITLE:

Production of Ketones Having a Tin Atom in α -Position Relative to the Carbonyl Group (Polucheniye ketonov, soderzhashchikh atom olova v α -polozhenii k karbonil'noy gruppe)

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 124, Nr 5, pp 1073-1075 (USSR)

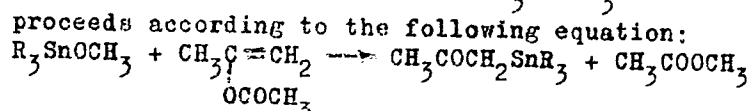
ABSTRACT:

The authors have continued their investigation of the simplest metal enolates (Ref 1) and have attempted to produce them by an exchange reaction between the metal alcoholates and the acetates of the enol forms. The present paper sets forth the investigation results of the interaction of the enol acetates with the trialkyl methoxy-stannates. When equivalent amounts of R_3SnOCH_3 and enol acetate are poured together the reaction mixture will show a moderate temperature rise and alkyl acetate (quantitatively) and tin-organic compounds (yield 70-95 %) can be distilled from it. These latter, however, are no trialkyl tin-enolates but their isomeric α -metallized ketones. The question whether the tin-organic compound which has been formed from isopropenyl acetate and R_3SnOCH_3 has a ketone or

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Production of Ketones Having a Tin Atom in α -Position SOV/20-124-5-31/62
Relative to the Carbonyl Group

enol structure can be answered with the aid of the infrared and Raman spectra in two ranges (1,600-1,700 and $\sim 3,000 \text{ cm}^{-1}$) (this has been found with the assistance of B. V. Lokshin, Mrs. L. A. Kazitsyna, and Mrs. Ye. G. Treshchova). It has been found that the reaction between R_3SnOCH_3 and the enol acetates



It can be formally considered an attachment of a tin compound to the double bond. The constants, yields, and analyses are shown in table 1. This new class of organometallic ketones having a tin atom in α -position is clearly distinguished from ketones having an R_3Sn group in β -position (Ref 2). There are 1 table and 3 references, 1 of which is Soviet.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova
(Moscow State University imeni M. V. Lomonosov)

SUBMITTED: November 25, 1958
Card 2/2

5(3)

SOV/2c-124-6-19/55

AUTHORS:

Nesmeyanov, A. N., Academician, Lutsenko, I. P., Krayts, Z. S.,
Bokovoy, A. P.

TITLE:

The Vinyl Esters of Phosphorous Acid (Vinilovyye efiry fosfori-
stoy kisloty)

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 124, Nr 6,
pp 1251 - 1254 (USSR)

ABSTRACT:

The known representatives of the unsaturated esters of phosphorous acid, which are not numerous, are compounds of the allyl series (Refs 1,2). As far as the general methods of synthesis of these esters cannot be used for the production of the acid mentioned in the title not one representative of vinyl esters of this acid is known. In order to be able to investigate the conditions and the isomerization direction the authors have produced both, compounds of the series $(RO)_2POCH = CH_2$ and $ROP(OCH = CH_2)_2$ and trivinyl phosphate. For this purpose they used the acylation reaction of α -monomer-curized oxo-compounds (Ref 3) which as it is known proceeds by transfer of the reaction center. Although chloro-mercuri

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The Vinyl Esters of Phosphorous Acid

SOV/20-124-6-19/55

acetaldehyde reacts with diethyl-chloro phosphite already in the cold, the yields in vinyl esters are very small since it is a well-known fact that esters of phosphorous acid react with sublimate (Ref 4). In order to avoid this difficulty the authors carried out a reaction of diethyl-chloro phosphite with mercuri bisacetaldehyde in isopentane. The reaction was, however, not carried out until the formation of the sublimate but only until the formation of chloro-mercuri acetaldehyde. In this connection dialkyl vinyl phosphite was obtained in a yield of about 40%. It was of advantage to add not more than 0.1 mole of the mercury-organic compound and the amine into the reaction vessel at once. After the addition of an equivalent amount of chlorine phosphite the next portion of the two substances initially mentioned is added. In connection with the synthesis of alkyl vinyl phosphite from Menshutkin chloric anhydride and mercuri bisacetaldehyde already at the beginning of the reaction a strong polymerization takes place. This polymerization can be suppressed by the addition of an equivalent quantity of bases and the alkyl divinyl esters may be obtained in a 50-60% yield. The interaction of dialkyl-chloro

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The Vinyl Esters of Phosphorous Acid

SOV/20-124-6-12/55

phosphite with mercuri bisacetaldehyde in the presence of a base leads to still higher yields in dialkyl vinyl phosphites (60-70%). In all cases triethyl amine was used as base, except for the case of methyl derivatives for the synthesis of which diethyl aniline was used. Trivinyl phosphite was produced from phosphorus trichloride in a similar way. Finally, the properties and reactions of vinyl phosphites are described. An experimental part gives the usual data. There are 1 table and 4 Soviet references.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova
(Moscow State University imeni M. V. Lomonosov)

SUBMITTED: November 25, 1958

Card 3/3

(3)
 AUTHORS: Nesmeyanov, A. N., Academician, SOV/20-125-1-25/67
 Rybinskaya, N. I.
 TITLE: Synthesis of the 2,8-Diaryl-1,9-diaza-dehydroquinolizinium
 Salts (Sintez soley 2,8-diaril-1,9-diazadegidrokhinoliziniya)
 PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 125, Nr 1, pp 97-100
 (USSR)
 ABSTRACT: The authors investigated the possibilities of producing a new
 aromatic heterocyclic system, of the cation 1,9-diaza-
 dehydroquinolizinium (pyrimido-(1,2-a)-pyrimidinium) by the
 interaction of 2-aminopyrimidines with β -chlorovinylketones.
 Actually, salts of the substance mentioned in the title form
 in the condensation of aryl- β -chlorovinylketones with
 4-aryl-2-aminopyrimidines under the action of the 70% perchloric
 acid in the methanol medium. The initial 4-aryl-2-amino-
 pyrimidines were produced from aryl- β -chlorovinylketones and
 guanidine (Ref 4). The cation mentioned in the beginning is a
 condensed aromatic system of 2 pyrimidine nuclei with a common
 ammonium-nitrogen atom. In consequence of the interaction
 carried out 4 salts of the 1,9-diaza-dehydroquinolizinium

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Synthesis of the 2,8-Diaryl-1,9-diaza-
dehydroquinolizinium Salts

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can be expected: The authors succeeded in isolating only one of them (A). The position of the substituents was checked; in this connection 2 different salts A_1 and A_2 formed. One of them had to be selected. It was found that the salt is subject to a rupture of cycle under the influence of 5% NaOH. For this reason only the salt A_2 can be used. Thus, a structure of the perchlorates of 2,8-diaryl-1,9-diaza-dehydroquinolizinium must be ascribed to those salts which are formed due to condensation of 4-aryl-2-aminopyrimidine with aryl- β -chlorovinylketones. The proof mentioned in the paper holds only if the assumed and very probable presupposition that the condensation of different aryl- β -chlorovinylketones and 4-aryl-2-aminopyrimidines takes place in the same way, is correct. An experimental part gives the usual data. There are 1 figure, 1 table, and 5 references, 4 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR
(Institute of Elemental-Organic Compounds of the Academy of Sciences, USSR)

SUBMITTED: October 21, 1958
Card 2/2

5(2,3)

AUTHORS:

Nesmeyanov, A. N., Academician,
Tolstaya, T. P., Isayeva, L. S.

SOV/20-125-2-25/64

TITLE:

Reactions of the Salts of Diphenyl-bromonium, Diphenyl-chloronium, and Triphenyl-oxonium With Metals (Reaktsii soli y difenilbromoniya, difenilkhloroniya i trifeniloksoniya s met. iami

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 125, Nr 2, pp 330-332 (USSR)

ABSTRACT:

Aryl-diazonium- (Ref 1) and di-aryl-iodonium salts (Ref 2) react with metals to form organometallic compounds of the non-transitional metals. The paper under consideration is devoted to the reactions with metals of the salts discovered by the author and enumerated in the title (Refs 3-5). Acetone constitutes the best medium for the formation of organometallic compounds from aryl-diazo compounds. It was mainly employed in the experiments under consideration. Tables 1 and 2 show the results. The reactions with metals of the diphenyl-bromonium salts and of the similarly behaving diphenyl-chloronium salts resemble those of the diphenyl-iodonium- and phenyl-diazonium salts. In certain cases (dealt with in greater detail in the paper), they form organometallic com-

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Reactions of the Salts of Diphenyl-bromonium,
Diphenyl-chloronium, and Triphenyl-oxonium With Metals

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pounds of the nontransitional metals, yields being satisfactory in many instances. The triphenyl-oxonium salts, however, could not be induced to effect this formation. There is a far-reaching analogy in the behaviour of the salts of all 3 diphenyl-halogenoniums on the one hand, and of the phenyl-diazonium salts on the other hand. For this reason, the authors returned to the interaction of the diazonium salts with bismuth. They were able to propose a preparative manufacturing procedure for triaryl-bismuth compounds by means of the diazo method (Ref 7), which is vastly superior to the methods described on earlier occasions (Ref 8). There was a significant discrepancy in the behaviour of the halogenides (usually iodides) of the diphenyl-halogenoniums on the one hand, and of their borofluorides on the other hand. The former reacted less frequently with metals to form organometallic compounds (Hg, Sn). Unlike the borofluorides, they did, however, form phenyl-mercury-halogenides with good yields. With nontransitional metals, said borofluorides formed organometallic compounds. With nobler metals (Pt, Ag, Hg), however, the reaction did not occur. The halogenides also reacted with Pt and Cu. In the former case, due to a purely catalytic

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Reactions of the Salts of Diphenyl-bromonium,
Diphenyl-chloronium, and Triphenyl-oxonium With Metals

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reaction, a mixture of haloide benzenes was formed. The above-stated facts can best be illustrated by a simple, though by no means exhaustive, pattern (given in this connection, (reaction groups I and II, Ref 9). The hypothesis behind the pattern takes for basis the homolytic disruption of the bonds of the covalent form of the onium compound, which leads to the formation of an organometallic compound. The reaction group II is explained in references 2 and 10. Group I is based on the notion that an interaction takes place between the metal as a nucleophile reagent and the cations of diphenyl-halogenonium and diphenyl-diazonium (their borofluoric salt). By way of conclusion, the authors furthermore try to substantiate this hypothesis, and to predict its consequences. There are 2 tables and 16 references, 10 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR
(Institute of Elemental-organic Compounds of the Academy of Sciences USSR). Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosova)

Card 3/4

5(3)

AUTHORS: Nesmeyanov, A. N., Academician, SOV/20-125-5-23/61
Kazitsyna, L. A., Lokshin, B. V., Vil'chevskaya, V. D.

TITLE: Infrared Spectra of Some Alkyl- and Arylferrocenes
(Infrakrasnyye spektry nekotorykh alkil- i arilferrotsenov)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 125, Nr 5,
pp 1037-1040 (USSR)

ABSTRACT: It was proved earlier that frequencies within the range of 1000 and 1100 cm^{-1} in the infrared spectrum of ferrocene derivatives may be indicative of the presence of a cyclopentadienyl ring free from substituents (Refs 1, 2). The next problem to be solved is the determination of the mutual position of the substituting groups in a ring of the homoannular disubstituted ferrocene derivatives. The authors succeeded in obtaining 1.2.- and 1.3-isomers according to these spectra for acetylethyl- and ethyl-dimethyl ferrocene. However, the attempts which were made to use the derived rules for other homoannular disubstituted ferrocenes failed. The authors investigated the infrared spectra of

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Infrared Spectra of Some Alkyl- and Arylferrocenes

SOV/20-125-5-23/61

some substituted ferrocenes within the range of the NaCl-prism (Table 1). It was reported (Ref 1) that the spectra of two diethyl-ferrocenes (n_D^{20} 1.5820 and 1.5847) differ only by the frequency 1277 cm^{-1} , which is observed in one spectrum only. Since either spectrum exhibits absorption within the range of 1000 and 1100 cm^{-1} (which indicates a free cyclopentadienyl ring), their structure has to be either 1.2- or 1.3-diethyl-ferrocene. Absorption within the range of 1280 cm^{-1} is observed in all monosubstituted alkyl-ferrocenes (except methyl-ferrocene), phenyl-ferrocene, and all alkyl- and aryl-ferrocenes disubstituted in various rings, and, finally, in homoannular di-isopropyl and di-tert-butyl-ferrocenes. In the case of the last-mentioned substances a 1.3-structure is more probable, due to steric considerations. However, absorption within the range of 1280 cm^{-1} is lacking in constantly 1.2-substituted homoannular ferrocenes (substances Nr 11 - 13, Table 1), in which a 1.2-position of the substituents results from their

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Infrared Spectra of Some Alkyl- and Arylferrocenes

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bicyclic structure. The synthesis of the compounds 11 and 12 was given earlier (Ref 9). The synthesis of Nr 13 is described in the present paper. The data discussed here render the assumption probable that the absorption within the range of 1280 cm^{-1} is owing to the presence of two carbon atoms of ferrocene. These atoms are not substituted and adjacent to a carbon atom of ferrocene to which a hydrocarbon radical is bound. The occurrence of these bands in the spectra of homoannular disubstituted ferrocenes indicates the 1,3-position of the substituents. There are 1 table and 12 references, 8 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR
(Institute of Elemental-organic Compounds of the Academy of Sciences, USSR)

SUBMITTED: January 30, 1959

Card 3/3

5(2)

AUTHORS:

~~Nasmevanov~~, A. N., Academician,
Reutov, O. A., Corresponding Member
AS USSR. Tolstaya, T. P., Ptitsyna, O. A.,
Izayeva, L. S., Turchinskiy, M. F.,
Bochkareva, G. P.

SOV/20-125-6-25/61

TITLE:

Organometallic Compounds Prepared From Double Salts of Halogen Metals and Halogenoniums (Metalloorganicheskiye soyedineniya iz dvoynnykh soley galoidnykh metallov i galogenoniyev)

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 125, Nr 6, pp 1265-1268 (USSR)

ABSTRACT:

The present paper adds two further types, (III) and (IV), to the two rather similar reaction types (I) and (II) of the synthesis of organometallic compounds. Hg, Tl, Sn, Pb, As, Sb, and Bi may appear as metal $M^{(n)}$ in the method of diazonium double salts (Ref 1); Cu, Zn, Fe, as well as $M^{(p)} - M^{(n)}$ as metal $M^{(p)}$ for various combinations. In the method of iodonium double salts (Ref 2) Hg, Sn, Sb, and Bi were investigated as $M^{(n)}$ which gave a good yield of corresponding organometallic

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Organometallic Compounds Prepared From Double Salts
of Halogen Metals and Halogenoniums

SOV/20-125-6-25/61

compounds. The same metal $M^{(n)}$ is usually used as $M^{(p)}$, sometimes, however, Zn or Cu. The corresponding decomposition reactions were carried out by the authors in an acetone solution. For this purpose the same metal powder was used as was chosen by O. A. Reutov and O. A. Ptitsyna for diphenyl iodonium salts. The course and the results of these new reactions were found to be completely similar to those of the last-mentioned salts. This is a new confirmation of a similarity of all diaryl halogenoniums. Phenyl mercury iodide with yields of 22 and 35% is produced by decomposition of the double salts of diphenyl chloronium iodide and of diphenyl bromonium iodide with HgJ_2 by powdered copper in acetone at low temperature. Diphenyl-tin-dichloride with yields of 57 and 55% is produced by decomposition of the double salts of diphenyl chloronium- and diphenyl bromonium with $SnCl_4$ by powdered tin. The decomposition of the corresponding double salts of antimony powder leads to a mixture of phenyl-dichlorostibine, diphenyl-chlorostibine, and a small quantity of organo-antimony triaryl compounds. Triphenyl bismuth is produced by decomposition of the bismuth-trichloride

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Organometallic Compounds Prepared From Double Salts
of Halogen Metals and Halogenoniums

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double salts by bismuth powder. According to the analysis it is assumed that the double salts of antimony-trichloride and of bismuth-trichloride form mixtures of the compounds:

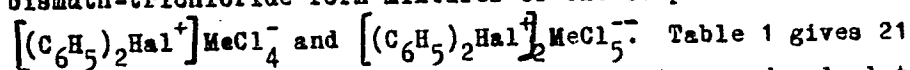


Table 1 gives 21 decomposed salts, the decomposition temperature and calculated as well as actually obtained results of the analysis, table 2 shows the decomposition reactions of the aforesaid double salts with the halides of heavy metals. The double salts of triphenyl-oxonium either do not react at all with the metal powders under the given experimental conditions, or only with a change of the anion part of the double salt. The cation of triphenyl-oxonium is not changed and does not form organometallic compounds. Thus this method is restricted by the inapplicability of oxonium- and (as is expected by analogy) of ammonium salts. The authors finally try to explain this behavior of triphenyl-oxonium salts. There are 2 tables and 11 references, 5 of which are Soviet.

ASSOCIATION:
Card 3/4

Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova
(Moscow State University imeni M. V. Lomonosov) Institut

Organometallic Compounds Prepared From Double Salts
of Halogen Metals and Halogenoniums

SOV/20-125-6-25/61

elementoorganicheskikh soyedineniy Akademii nauk SSSR (Institute
of Elemental-Organic Compounds of the Academy of Sciences USSR)

SUBMITTED: January 7, 1959

Card 4/4

5 (3)

AUTHORS:

Nesmeyanov, A. N., Academician,
Kochetkova, N. S.

SOV/20-126-2-22/64

TITLE:

Pentaethano-diferrocene (Pentaetanodiferrotsen)

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 126, Nr 2,
pp 307-309 (USSR)

ABSTRACT:

The authors have realized the reciprocal effect of ferrocene with a great excess of 1,2-dichloro ethane without foreign solution. This forms a continuation of the study of ferrocene alkylation under the conditions of the Friedel-Crafts reaction with halogen-alkyls and alkylenes. Now, instead of differoceny-ethane and relatively high molecular resins (which have a structure of several ferrocene nuclei, due to there being connected by $\text{CH}_2\text{-CH}_2$ -bridges) they obtained a series of polyethane-polyferrocenes. These contained no halogen, are soluble in chloroform and benzene, but not in methanol. They differ from each other by their solubility in ether. This different solubility was utilized in separating the reaction mass in individual substances. The substance with the least molecular weight, with a decomposition-temperature of 130° ,

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Pentaethano-diferrocene

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contained, according to the analysis, 2 ferrocene nuclei and 5 ethane bridges. Its molecular weight proved, that it was the substance named in the title. According to the infra-red spectrum, this substance can only have the structure of model (I). A further proof is the density, compared with ferrocene, which indicates a very dense packing of the carbon atoms in molecule. The substance under review at room temperature exhibits no Debyeogram of a crystalline substance. This can be caused by an arbitrary mutual orientation of the tunnel-shaped molecules along axis. Time consuming investigations will be necessary to prove the structure of the aforementioned substance chemically. According to provisional results, its brominating lead to pentabromo-cyclopentane. The polyethane-ferrocenes, with a higher (about 1000 and 2000) molecular weight can be isolated through fractionated precipitation with methanol. They are less soluble in ether and contain 4 or 8 ferrocene residues. According to the analysis they are closely connected to the firstmentioned substance and produce possibly 2 and 4 similar molecules which are bound by ethane bridges. This is confirmed by infra-red spectra. There follows, finally, an experimental part, entitled F e r r o c e n e

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Pentaethano-diferrocene

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a n d D i c h l o r o e t h a n e . The theoretical calculation of the density of the substance I was made by O. V. Starovskiy, under the supervision of Prof. A. I. Kitaygorodskiy. Infra-red spectra were measured by N. A. Chumayevskiy in the laboratory of I. V. Obreimov, Academician. There are 1 figure and 4 references, 3 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR
(Institute of Elemental-organic Compounds of the Academy of Sciences, USSR)

SUBMITTED: January 8, 1959

Card 3/3

5 (2,3)

AUTHORS:

Nesmeyanov, A. N., Academician,
Sazonova, V. A., Drozd, V. N.

SOV/20-126-5-25/69

TITLE:

Ferrocenyl Boric Acid and 1,1' Ferrocenylene-Diboric Acid and
Their Reactions (Ferrotsenilbornaya i 1,1'-ferrotsenilendi-
bornaya kisloty i ikh reaktsii)

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 126, Nr 5, pp 1004 - 1006
(USSR)

ABSTRACT:

The authors have obtained a mixture of the two acids mentioned
in the title by the action of a mixture of lithium and dili-
thium-ferrocene (Ref 1) on boron-n-butyl-ester. They were ex-
tracted by alcalies out of the reaction mixture. Their separa-
tion is explained by the high degree of solubility of the mono-
-acid and the insolubility of the diboric acid in ether. With
respect to its chemical properties the mono-acid is similar to
arylboric acid. Thus, ferrocene is obtained by hydrolysis in
the presence of $ZnCl_2$; with sublimate ferrocene-mercury chlor-
ide is easily formed (Ref 1), whilst with cupric chloride and
cupric bromide chlorine-ferrocene and bromine ferrocene are
formed (Ref 2). In the same manner also the dihalogen-ferrocene

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**Ferrocenyl Boric Acid and 1,1' Ferrocenylene-
Diboric Acid and Their Reactions**

SOV/20-126-5-25/69

derivates are produced from the diboric acid mentioned in the title. Thus, all three mono-halogen-ferrocenes: chlorine-, bromine-, and iodine-ferrocene are known, as well as all three hetero-annular dihalogen ferrocenes. The present investigation has revealed the properties of the dibromo ferrocene which was obtained in a purer crystalline form under the action of the ferrocenylene diboric acid. Under the interaction of ferrocenyl-boric acid and of an ammoniacal silver oxide solution, ferrocene and diferrocenyl are produced, whilst for the phenyl boric acid a hydrolysis up to benzene under the action of this reagent and for the alkyl-boric acids a doubling of the radical and a disproportioning of the latter had been known. There are 2 Soviet references.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova
(Moscow State University imeni M. V. Lomonosov)

SUBMITTED: April 16, 1959

Card 2/2

5 (2)

AUTHORS:

Nesmeyanov, A. N., Academician,
Kazitsyna, L. A., Lutsenko, I. F.,
Rudenko G. A.

SOV/20-127-1-30/65

TITLE:

A Spectroscopic Investigation of α -Metalated Aldehydes..
and Ketones and Lithium Vinylate (Spektroskopicheskoye issle-
dovaniye α -metallirovannykh al'degidov i ketonov i vinilata
litiya)

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 1, pp 115 - 116
(USSR)

ABSTRACT:

The α -mercurized aldehydes and ketones are able to react in two
ways (at C and O) and to form two series of derivatives (Refs
1-3). Either compounds are formed by the direct substitution of
an Hg-atom (reaction with triphenyl-chloro-methane), or (as
e.g. in the case of the reaction with acid halides) the reac-
tion center shifts in consequence of a distinctly marked con-
jugation of the Hg-C and C=O bonds (σ - π - conjugation).
The above-mentioned conjugation is distinctly marked in the
substances mentioned in the title due to the presence of a me-
tal atom with comparatively high polarizability (Hg, Sn).
Changes in the absorption bands of the carbonyl group of these

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A Spectroscopic Investigation of α -Metalated
Aldehydes and Ketones and Lithium Vinylate

SOV/20-127-1-30/65

compounds in the oscillation- and electron spectra can therefore be expected. The authors investigated the ultraviolet- and infrared spectra of eight mercurized carbonyl compounds and of two ketones which contain Sn-atoms in α -position to the C=O group. Table 1 shows that the frequencies of the carbonyl group in the infrared spectrum are in fact considerably shifted under the influence of the Hg-atom (Ref 4). Table 2 shows the absorption maxima of the same compounds in the ultraviolet light, furthermore, those of acetaldehyde, isobutyric aldehyde, and acetone for comparison. An intense absorption band within the range (280-300 m μ) occurred in these spectra of the Hg- and Sn-derivatives of the oxo-compounds, which is characteristic of carbonyl compounds; intensity increased by 200-300 times. The above-mentioned data confirms again the existence of an σ - π -conjunction in the compounds mentioned as can be proved as well by several chemical reactions. Furthermore, the ultraviolet- and infrared spectra of a very simple metal enolate were investigated, the structure of which is isomeric to that of RCOCH_2Me (1). Lithium vinylate (Ref 6) was investigated. Ab-

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**A Spectroscopic Investigation of α -Metalated
Aldehydes and Ketones and Lithium Vinylate**

SOV/20-127-1-30/65

sorption bands of the carbonyl group lacked here completely. A moderately intense band which corresponded to the C=C double bond was, however, found to occur in the infrared spectrum at 1610 cm^{-1} . It was considerably shifted due to metal influence, which is well in line with the shifting of the double bond conjugated with a phenyl- or carbonyl group (Ref 4). This confirms earlier conclusions concerning the C-structure of the organo-mercury compounds obtained by the addition of Hg acetate to ether and ester as well as concerning the O-structure of the cleavage product of mercury-bis-acetaldehyde by alkali metals. There are 2 tables and 6 Soviet references.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova
(Moscow State University imeni M. V. Lomonosov)

SUBMITTED: April 20, 1959

Card 3/3

5 (3)

AUTHORS:

Nesmeyanov, A. N., Academician, SOV/20-127-2-30/70
Karapetyan, Sh. A., Vasil'yeva, Ye. I., Freydlina, R. Kh.,
Corresponding Member AS USSR

TITLE:

Separation and Properties of Higher $\alpha, \alpha, \alpha, \omega$ -Tetrachloro Alkanes

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 2, pp 345-347 (USSR)

ABSTRACT:

Telomer mixtures are formed in the ethylene telomerization with CCl_4 from which the substances mentioned in the title were isolated and described in individual form. They contain up to 15 carbon atoms (Refs 1-3). The authors investigated the conditions of the vacuum rectification of these substances at a pressure of 0.2-0.5 mm and obtained pure telomers which have up to 23 C-atoms in one molecule. The rectification column used for this purpose is described. The mentioned tetrachloro alkanes were obtained from a telomer mixture from the plant of the Kaluzhskiy kombinat sinteticheskikh i natural'nykh dushistykh veshchestv (Kaluga Kombinat of Synthetic and Natural Aromatics) (Ref 5). The pressure amounted to 150 atmospheres absolute pressure and the molar ratio between ethylene and CCl_4 was approximately 20 : 1.

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A technical telomer mixture always contains traces of metal

Separation and Properties of Higher $\alpha, \alpha, \alpha, \omega$ -Tetrachloro SOV/20-127-2-30/70
Alkanes

chlorides which accelerate the dehydrochlorination of tetrachloro alkanes, especially at 160° and higher temperatures (Ref 6). The calcined soda (5%) added during the distillation transforms the metal chlorides into less active basic salts. This reduces rapidly the catalytic decomposition of the tetrachloro alkanes. The isolation of telomers above C₁₅ is difficult even with an addition of soda. Therefore the tetrachloro alkanes were extracted by ethyl alcohol and acetone under utilization of their different solubility in organic solvents (Ref 2) after C₅ - C₉ had been distilled off. They contained the telomers C₁₇ and C₂₅. Substances isolated in the first rectification were a second time distilled off on the same column in order to obtain the individual telomers (Table 1). Figure 1 shows the rules governing the changes of boiling temperature for the entire series of tetrachloro alkanes from C₅ - C₂₃. Figure 2 gives in a diagram the dependence of the densities and the molar volumes on the molecular weight of these substances. The molar volumes of the mixtures of tetrachloro alkanes are additive within a wide range. Their

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Separation and Properties of Higher $\alpha,\alpha,\alpha,\omega$ -Tetrachloro Alkanes SOV/20-127-2-30/70

viscosity was determined only for lower telomers (Ref 7) (Table 1, Fig 3 - determinations of L. M. Shulov). Yu. P. Chizhov carried out the fractionated distillation (Fig 4) in the determination of the physical constants (Table 1). There are 4 figures, 2 tables, and 8 references, 6 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR (Institute of Elemental Organic Compounds of the Academy of Sciences, USSR)

SUBMITTED: May 9, 1959

Card 3/3

5(3)
AUTHORS: Nesmeyanov, A. N., Academician, Freydlina, R. Kh., Corresponding Member, AS USSR, Petrova, R. G., Terent'yev, A. B.

SOV/20-127-3-26/71

TITLE: Reaction Between 1,1,1-Trichloropropene and Mercaptans

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 3, pp 575 - 577 (USSR)

ABSTRACT: At least 3 types of addition reactions (Ref 1) are known for 1,1,1-trichloropropene: a) electrophilic addition (of hypobromous acid, for example; this reaction takes place in contrast to the Markovnikov law); b) nucleophilic addition, occurring together with a re-arrangement of allyl, and finally c) radical addition; this takes place together with a re-arrangement of the meanwhile developed radicals, from type "A" to type "B" (see Scheme). The addition of thiophenol and benzyl mercaptan was investigated in the present work by means of 1,1,1-trichloropropene. 2,3,3-trichloropropylphenylsulphide (see Scheme) developed by means of an addition of the first mentioned substance (and an exposure to the light of a 100 w bulb). Its structure was determined in two ways (Ref 2). Thus the reaction takes place under the given con-

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Reaction Between 1,1,1-Trichloropropene and
Mercaptans

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ditions, according to the homolytical mechanism. In the case of benzylmercaptan, however, 2 products develop: 2,3,3-trichloropropylbenzylsulphide (II) and 3,3-dichloropropene-2-yl-benzylsulphide (III). The latter compound is predominating. From the determination of the structure of the sulphides (II) and (III) by means of a different synthesis, it was found that HCl is separated during the reaction. Its amount corresponds to that of the produced sulphide (III) (see Scheme). The formation of sulphide (III) according to the method of a nucleophilic addition is less probable. 3,3,3-trichloropropylphenylsulphide developed during the reaction of 1,1,1-trichloropropene with thiophenol in the presence of sulphur as inhibitor of radical processes. Its structure was confirmed by the lacking of frequencies in the i.-r.-spectrum which are characteristic of the methyl group. There are 2 references, 1 of which is Soviet.

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Reaction Between 1,1,1-Trichloropropene and
Mercaptans

SOV/20-127-3-26/71

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk
SSSR (Institute for Elemental-organic Compounds of the Academy of Sciences, USSR)

SUBMITTED: May 6, 1959

Card 3/3

5 (2, 3)
AUTHORS:

Freydlina, R. Kh., Corresponding Member SOV/20-128-2-26/59
AS USSR, Kost, V. N., Khorlina, M. Ya., Nesmeyanov, A. N.,
Academician

TITLE: Addition of Hydrogen Bromide to 1,1,1,2-Tetrachloropropene-2
and 1,1,2-Trichloropropene-2 in the Presence of Benzoyl Peroxide

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 2, pp 316-319 (USSR)

ABSTRACT: The authors investigated the above topic in continuation of their
own previous papers (Refs 1, 2) as well as in cooperation with
L. I. Zakharkin (Ref 3) and A. B. Belyavskiy (Ref 4) on
rearrangements of free radicals. The interaction between HBr
and the substance mentioned first in the title led to a mixture
of products. 1,1,2,2-Tetrachloro-3-bromopropene (I) with a
yield of approximately 30% was isolated from the latter in
addition to other compounds (II) - (IV) (see Scheme). The
existence of (I) and (II) shows that the addition proceeds
here with a rearrangement of the type mentioned in references
1-4. The intermediate radicals are apparently comparatively
little stable and decompose under separation of a chlorine
atom. The yield of (I) is therefore low, and (II) - (IV) occur
in the reaction products. With respect to its composition,

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Addition of Hydrogen Bromide to 1,1,1,2-Tetrachloro- SOV/20-128-2-26/59
propene-2 and 1,1,2-Trichloropropene-2 in the Presence of Benzoyl Peroxide

constants, and infrared spectrum, substance I is identical with the 1,1,2,2-tetrachloro-3-bromopropane produced by the authors according to another scheme (see there), it differs, however, from the 1,1,1,2-tetrachloro-3-bromopropane produced by the chlorination of the $\text{CCl}_2=\text{CH}-\text{CH}_2\text{Br}$ with respect to constants and infrared spectrum. Ethyl cellosolve HCl is split off from substance I by treatment with alkalis, which results in the production of compound III. The latter was identified as hydrochloride of the diethyl-amine derivative $\text{CCl}_2=\text{CCl}-\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2 \cdot \text{HCl}$ (V). As far as constants and infrared spectrum are concerned, compound II corresponds to 1,1,2,2,3-pentachloropropane. Trichlorobromopropene III together with diethyl-amine and thiourea yields derivatives which were identified as hydrochloride and picrate respectively. When reacting with Hg, substance III yielded the trichloroallyl-mercury bromide which was identical with that produced by the usual method (Ref 5). As to its properties, tetrachloropropene IV corresponds to the well-known 1,1,2,3-tetrachloropropene, and together with diethyl-amine it yields the corresponding

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Addition of Hydrogen Bromide to 1,1,1,2-Tetrachloro- SOV/20-128-2-26/59
propene-2 and 1,1,2-Trichloropropene-2 in the Presence of Benzoyl Peroxide

derivative V. The addition of HBr to 1,1,2-trichloropropene-2 proceeds without rearrangement under formation of 1,1,2-trichloro-3-bromopropane (see Scheme). This reaction course is apparently connected with a greater stability of the radical A produced as against the radical $\text{CHClCCl}_2\text{CH}_2\text{Br}$ which might be produced by a rearrangement. As to its constants, composition, and infrared spectrum, substance VI, i.e. $\text{HCCl}_2 - \text{CHCl} - \text{CH}_2\text{Br}$, which was produced in the last-mentioned reaction, is identical with the 1,1,2-trichloro-3-bromopropane. The isothioureia derivative furthermore obtained as picrate is identical with the corresponding derivative synthesized from the well-known 1,1,2-trichloro-3-bromopropane. There are 8 references, 7 of which are Soviet.

SUBMITTED: June 5, 1959

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5(2, 3)
AUTHORS: Nesmeyanov, A. N., Academician, SOV/20-128-3-32/58
Lutsenko, I. F., Brattsev, V. A.

TITLE: Vinylloxysilanes

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 3, pp 551-554
(USSR)

ABSTRACT: At the 2nd All-Union Conference on the Practical Application of Organo-silicon Compounds (1958), S. I. Sadykh-Zade and A. D. Petrov (Ref 1), as well as N.P. Kharitonov, B.N. Dolgov and Yu.I. Khudobin (Ref 1) reported on their methods of synthesizing siliceous vinyl ethers, in which one silicon atom is directly bound to the ether oxygen. They had been unknown up to that time. All of the 4 investigators mentioned think that the reaction in their synthesizing methods between R_3SiH and enol proceeds according to the scheme:

$R_3SiH + R'C(OH)=R'' \rightarrow R''=C(R')OSiR_3 + H_2$. Both the first and second groups of investigators only obtained monovinyl ether. In principle, the simplest vinylloxysilanes $R_3SiOCH=CH_2$ cannot be produced either by the 1st or the 2nd method. The large difference in the boiling temperatures of the isomeric compounds produced by these two methods is striking. For the production

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Vinylloxysilanes

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of vinyl esters of the type under discussion, the authors used the reaction of mercurated aldehydes and ketones with chlorosilanes. In hydrocarbon media, it only proceeds with complete organo-mercuric derivatives of aldehydes and ketones, and ends with the stage of organo-mercuric salt. The said ethers are formed in yields from 70 to 90%. The method suggested facilitates the binding of 1 to 4 vinyloxy groups to one silicon atom. The vinylloxysilanes polymerize in storing. Their constants, yields and analytical data are shown in table 1. The infrared and ultraviolet spectra recorded confirmed the structure of the ethers. A reaction variant was found: in the presence of pyridine, the organo-mercuric salts of the oxo compounds also undergo the reaction (see Diagram). Not the triethylchlorosilane, but its complex reacts here with pyridine (see Diagram). This variant makes it possible to use various chloromercuric aldehydes and ketones in the synthesis of vinylloxysilanes. These initial substances are much better accessible than complete Hg-derivatives. Compounds with various numbers of vinyloxy groups can also be obtained. In this way, the authors synthesized tetra-(isopropenyloxy)-silane. The triethyl-isopropenyloxysilane synthesized by the authors has approximately the same constants as the isomeric compound ob-

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Vinyloxysilanes

SOV/20-128-3-32/58

tained by Sadykh-Zade and Petrov (Ref 1), but is different from the substance described by Kharitonov, Dolgov, and Khudobin. There are 1 table and 3 Soviet references. .

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova
(Moscow State University imeni M. V. Lomonosov)

SUBMITTED: June 15, 1959

Card 3/3

5 (2,3)
 "AUTHORS: Nesmeyanov, A. N., Academician, SOV/20-128-4-25/65
 Tolstaya, T. P.
 TITLE: Formation of a Diphenylbromonium Salt on the Decomposition
 of $C_6H_5N_2HgBr_3$
 PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 4, pp 726 - 727
 (USSR)
 ABSTRACT: Depending on conditions, Nesmeyanov found (Refs 1,2) 2 principal directions of decomposition of double salts of phenyldiazonium iodide and mercuric iodide. One of them is the automatic decomposition producing the last-mentioned double salt in a 10% yield. In the experiments then made on the automatic decomposition of double salts of other halides and the corresponding mercuric halide, no separation was possible so that this method - now found to be real - could not be used at that time. But now the authors indicate that the automatic decomposition of $C_6H_5N_2HgBr_3$ proceeds in a way similar to that of the corresponding iodine compound. It causes the formation of a double salt of diphenylbromonium bromide and mercuric bromide (see Diagram). The latter reaction probably proceeds via bromo-

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Formation of a Diphenylbromonium Salt on the
Decomposition of $C_6H_5N_2HgBr_3$

SO7/20-128-4-25/65

benzene as an intermediate which is subsequently phenylated at the expense of a heterolysis of a new portion of $C_6H_5N_2HgBr_3$. This explains the small yield (2.5%) of diphenylbromonium salt. Hence, it appears that a former explanation by Nesmeyanov (Ref 1) should be replaced by a new one: the primary decomposition product - iodobenzene - is phenylated due to the heterolytic decomposition of $C_6H_5N_2HgJ_3$. The double salt of diphenylbromonium bromide and mercuric bromide was obtained from the diazonium double salt by addition of mercuric-bromide solution in hydrobromic acid to a phenyldiazonium-bromide solution until complete precipitation. 95 g of the double salt produced were subjected to decomposition at room temperature for several months. The 3rd reaction product - mercuric bromide - was obtained in a 74% yield. There are 4 references, 3 of which are Soviet.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova
(Moscow State University imeni M. V. Lomonosov)

SUBMITTED: July 2, 1959
Card 2/2

66174

SOV/20-128-5-28/67

5(2,5) 5.3700(B)

AUTHORS:

Nesmeyanov, A. N., Academician, Nogina, O. V., Dubovitskiy, V. A.

TITLE:

Activation Energy of the Disaggregation Process of Associated Titanium Alkoxy Derivatives

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 5, pp 964 - 965 (USSR)

ABSTRACT:

The association degree of these derivatives decreases comparatively slowly in diluted benzene solutions. Within several hours all associates disappear (Ref 1). The association of these derivatives is explained by intermolecular coordination bonds between the oxygen atoms of one molecule and the titanium atoms of the adjacent molecules. (Refs 2-5). The dependence of this phenomenon on temperature was investigated and the activation energy of disaggregation determined in this paper. The method of cryoscopy was used for this purpose. Figure 1 shows the kinetic curves of the disaggregation process of the associates of tetra-n-propoxy titanium at various temperatures. The values of activation energy were computed from the dependencies of the initial velocities on temperature (Fig 2). They are 7.7 kcal/mol for tetra-n-propoxy titanium, 8.0 kcal/mol ✓

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Activation Energy of the Disaggregation Process of
Associated Titanium Alkoxy Derivatives

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for associated tetraethoxy titanium, and 8.1 kcal/mol for di-n-propoxy titanium oxide. Limit concentration at which the association degree of titanium alkoxy derivatives decreases to 1 depends little on the structure of the titanium compound (Fig 3). The structure of the alkyl, however, has a distinct effect on this phenomenon. Spatial obstacles influence the association degree of the titanium derivatives mentioned. Association does not take place at all if there is a ramified carbon chain of tetraalkoxy titanium at the carbon atom adjacent to titanium (tetraisopropoxy titanium, tetratertiary butoxy titanium, references 2,6) in the case of concentrations of benzene solutions up to 2.0 mol%. If the ramification of the alkyl chain in tetraalkoxy titanium occurs on the β -carbon atom, the tetraalkoxy titaniums are associated in benzene solutions. Also in this case the association degree decreases gradually and reaches 1 after several hours. There are 3 figures, and 6 references, 1 of which is Soviet.

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Activation Energy of the Disaggregation Process of
Associated Titanium Alkoxy Derivatives

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SOV/20-128-5-25/67

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk
SSSR (Institute of Elemental-organic Compounds of the Academy
of Sciences, USSR)

SUBMITTED: July 9, 1959

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5.3700(B)

5(3)

SECRET

SOV/20-129-5-27/64

AUTHORS: Nesmeyanov, A. N., Academician, Sazonova, V. A., Drozd, V. N.

TITLE: Oxyferrocene

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 129, Nr 5,
pp 1060 - 1063 (USSR)

ABSTRACT: No oxy-derivative of ferrocene has been hitherto known. The authors obtained oxyferrocene in two ways, namely, by way of ferrocenyl acetate: 1) by mixing aqueous solutions of ferrocenyl boric acid (Ref 3) with copper acetate, ferrocenyl acetate (yield 59%) and diferrocenyl (21%) are obtained, ferrocenyl propionate and diferrocenyl are formed with copper propionate (see Scheme); 2) ferrocenyl acetate was formed on heating bromo-ferrocene with copper acetate. The ferrocenyl acetate structure was confirmed by the reaction with phenyl magnesium bromide (see Scheme). The methyl diphenyl carbinol sample obtained in this connection melts with pure methyl-diphenyl-carbinol without a reduction in the melting point. Ferrocenyl benzoate was separated from the oxyferrocene yield after benzylation. Oxy-ferrocene (ferrocenol) is easily separated from alkaline solutions.

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Oxyferrocene

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much like phenol, on bubbling CO₂ through them. Oxyferrocene is a yellow crystalline air-unstable substance. It can be recrystallized from water (with quick heating), but becomes somewhat darker. It is soluble in ether, alcohols and chloroform. Moreover, the authors obtained the following derivatives of oxyferrocene: ferrocenyl benzoate, ferrocenyl ester of benzene sulfonic acid as well as oxyferrocene methyl ether (Table 1). All ethers and esters are crystalline substances which readily solve in organic solvents. Further properties of oxy-ferrocene are being investigated. There are 1 table and 5 references, 2 of which are Soviet. 4

SUBMITTED: September 11, 1959

Card 2/2

YEPIFANOVA, A.P.; NESMEYANOV, A.N., akademik, glavnyy red.; TOPCHYEV,
A.V., akademik, zamestitel' glavnogo red.; ISAKOVA, O.V., otv.
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(MIRA 13:6)

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glavnogo red.; ISAKOVA, O.V., otv.red.; LIKHTEINSTEYN, Ye.S.,
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ISAKOVA, O.V., otv.red.; LIKHTEINSKIY, Ye.S., otv.red.; SHUMKOV,
V.I., otv.red.; NIKITINA, O.G., red.izd-va; SUSHKOVA, L.A.,
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NESMEYANOV, A. N.

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PART I BOOK EXPLORATION		SCV/9346
<p>NESMEYANOV, A. N., ed. Spetsial'nyy kosmicheskii sluzhba (Space Stations; Collection of articles) Moscow, Izd-vo AN SSSR, 1960. 48 p. 25,000 copies printed. (Series: Akademiya nauk SSSR. Nauchno-populyarnaya seriya.)</p> <p>Ed.: A. N. Nesmeyanov; Compiler: V. V. Fedorov; Ed. of Publishing House: Ye. M. Klyuz; Tech. Ed.: I. D. Kovaleva. This book is intended both for the space specialist and the average reader interested in space problems. CONTENTS: The book contains 73 short articles by various Soviet authors on problems connected with space travel, the launch- ing of artificial earth satellites and the discussed. The ar- ticles were published in the period of 1957-1960. No person- alities are mentioned. There are no references.</p>		
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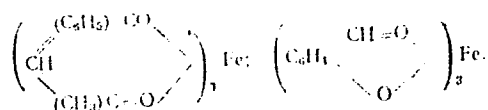
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SOV/62-60-1-10/37

AUTHORS: Freydina, R. Kh., Braynina, E. M., Nesmeyanov, A. N.

TITLE: Metathetical Reactions of Iron Chelates

PERIODICAL: Izvestiya Akademii nauk. Otdelenie khimicheskikh nauk, 1960, Nr 1, pp 59-62 (USSR)

ABSTRACT: Iron triacetylacetonate undergoes a metathetical reaction with benzoylacetone and salicylaldehyde, forming the corresponding iron chelates:

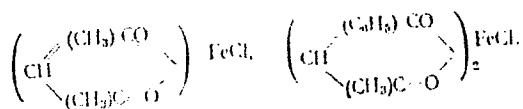


A reverse disproportionation takes place between ferric chloride and iron triacetylacetonate or iron tribenzoylacetone (molar ratio 1:2), forming the corresponding monochloroderivatives of iron:

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Metathetical Reactions of Iron Chelates

78064
SOV/62-60-1-10/37



One chelate radical is replaced by chlorine in the reaction of iron triacetylacetonate and iron tribenzoylacetonate with acetyl chloride. There are 5 references, 3 Soviet, 1 U.S., 1 German. The U.S. reference is: U.S. patent 2659711, Nov. 17, 1953.

ASSOCIATION: Institute of Element-Organic Compounds, Academy of Sciences, USSR (Institut elementoorganicheskikh soyedinenii Akademii nauk SSSR)

SUBMITTED: June 17, 1958

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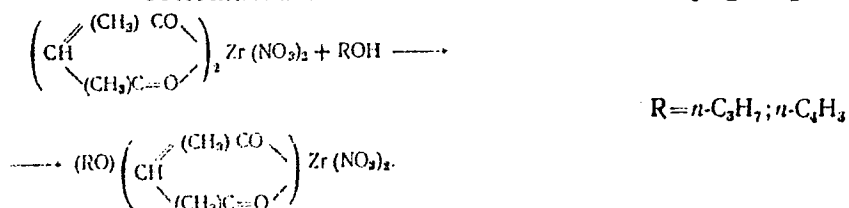
72065
SOV/62-60-1-11/37

AUTHORS: Braynina, E. M., Frydlina, R. Kh., Nesmeyanov, A. N.

TITLE: A New Method of Preparation of Alkoxyderivatives of Zirconium

PERIODICAL: Izvestiya Akademii nauk. Otdeleniye khimicheskikh nauk, 1960, Nr 1, pp 63-67 (USSR)

ABSTRACT: New zirconium derivatives were obtained, which contained both chelate- and alkoxy-groups:

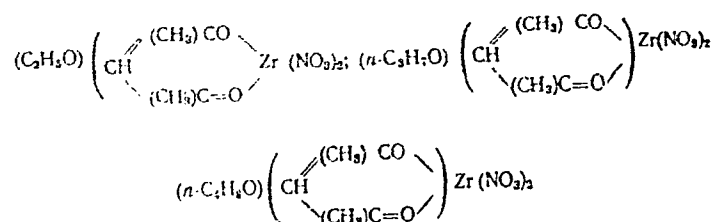


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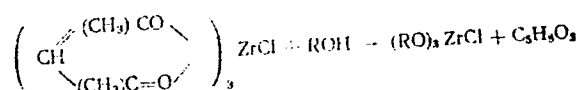
The following compounds were obtained:

A New Method of Preparation of
Alkoxyderivatives of Zirconium

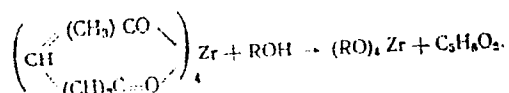
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SOV/62-60-1-11/37



Trialkoxyzirconium chlorides were obtained:



where R = propyl, butyl, hexyl, heptyl, octyl,
and nonyl (all normal). Alkyl orthozirconates
were prepared in the following manner:



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A New Method of Preparation of
Alkoxyderivatives of Zirconium

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where R = n-hexyl, n-heptyl, n-octyl and n-nonyl.
There are 6 references, 2 Soviet, 3 U.K., 1 U.S.
The 4 U.S. and U.K. references are: R. C. Mehrotra,
J. Am. Chem. Soc., 76, 226 (1954); D. C. Bradley,
Nature, 165, 75 (1950); the same, J. Chem. Soc.,
2025 (1953); the same, J. Chem. Soc., 3450 (1950).

ASSOCIATION: Institute of Element-Organic Compounds, Academy
of Sciences, USSR (Institut elementoorganicheskikh
soyedinenii Akademii nauk SSSR)

SUBMITTED: June 17, 1958

Card 3/3

5.3700

78090

SOV/67-60-1-50/21

AUTHORS: Nesmeyanov, A. N., Borisov, A. Ye., Novikova, N. V.

TITLE: Letter to the Editor. Geometrical isomers of Propenyl Compounds of Tri- and Pentavalent Antimony

PERIODICAL: Izvestiya Akademii nauk SSSR, otdeleniye khimicheskikh nauk, 1960, Nr 1, p 147 (USSR)

ABSTRACT: The authors report that during the study of stereochemistry of organometallics, a series of geometrical isomers of propenyl compounds of tri- and pentavalent antimony were synthesized, and that cis- and trans-propyllithium react with antimony trichloride to form corresponding cis- and trans-propylantimony. The reaction between these isomers and halogen lead to the formation of a series of isomers of pentavalent antimony:

$$(CH_3CH=CHCH_2CH_2)_3X, (CH_3CH=CHCH_2CH_2)_2CH_2SbX_2, X=Cl, Br, I.$$

cis- isomers, containing Cl and Br, are crystalline and

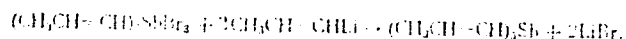
Card 1/2

Letter to the Editor. Geometrical Isomers
of Propenyl Compounds of Tri- and Penta-
valent Antimony

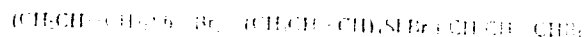
78090

SOV/62-60-1-36/31

the trans-isomers are liquids. Liquid geometrical
isomers of pentapropenylantimony were synthesized
from cis- and trans-isomers of tripropenylantimony
dichloride and the corresponding isomers of propenyl-
lithium:



These isomers have different refractive indices and
absorption spectra. They react with bromine, forming
two tetrapropenylantimony bromides:



There is 1 Soviet reference.

ASSOCIATION:

Institute of Element-Organic Compounds, Academy of
Sciences, USSR (Institut elementoorganicheskikh
soyedineniy Akademii nauk SSSR)

SUBMITTED:

October 29, 1959

Card 1/1

5.3700

78991
SOV/62-60-1-37/37

AUTHORS: Nesmeyanov, A. N., Borisov, A. Ye., Kovredov, A. I.,
Golubeva, Ye. I.

TITLE: Letter to the Editor. Reaction of Free Radicals With
Organomercury Compounds

PERIODICAL: Izvestiya Akademii nauk SSSR, otdeleniye khimicheskikh
nauk, 1960, Nr 1, p 148 (USSR)

ABSTRACT: The authors report that compounds $RHgR'$ react with CCl_4
in the presence of benzoyl peroxide to form compounds
shown in Table B. There are 1 table; and 2 references,
1 U.S. and 1 Soviet. The U.S. reference is: M. S. Kh
Kharasch, R. Marner, J. Am. Chem. Soc., 48, 5130 (1926).
ASSOCIATION: Institute of Element-Organic Compounds, Academy of
Sciences, USSR (Institut elementarnoorganicheskikh
soyedineniy Akademii nauk SSSR)

SUBMITTED: October 29, 1959

Card 1/3

Letter to the Editor. Reaction of Free
Radicals With Organomercury Compounds

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SOV/62-60-1-37/37

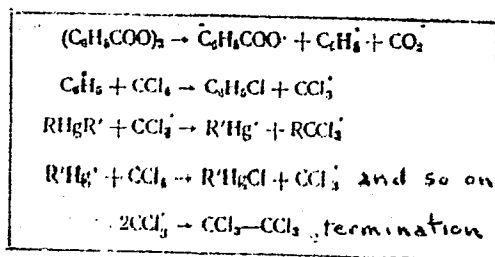


Table A

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B004/B066

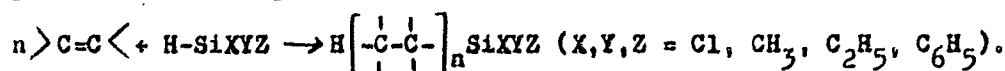
5.3700C

AUTHORS: Freydlina, R. Kh., Chukovskaya, Ye. Ts., Karapetyan, Sh. A.,
Nesmeyanov, A. N.

TITLE: Thermal Telomerization¹ of Olefins¹ With Silanes

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
1960, No. 4, pp. 662 - 668

TEXT: In previous papers (Refs. 1 - 3) it was proved that olefins are thermally telomerized with compounds containing a Si-H bond. The reaction proceeds according to the scheme:



The first experiments were performed in steel autoclaves. Since it was supposed that the metallic walls act as catalyst, the experiments were repeated in sealed glass tubes at 320 - 340°C and 50 atm. As may be seen from the data in Table 1, the results were the same as in the steel autoclaves. The thermal telomerization thus takes place without initiators

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Thermal Telomerization of Olefins With
Silanes

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B004/B066

or catalysts but is initiated by dissociation of the silane at the Si-H bond. The present paper reports on the influence of temperature and ethylene concentration upon the telomerization of C_2H_4 with methyl-dichloro silane (Table 2, Fig. 1). The same laws hold as for the telomerization of C_2H_4 with CCl_4 and $CHCl_3$ (Refs. 4 - 6). With increasing C_2H_4

content of the initial mixture the amount of low-boiling telomers decreases, that of the higher-boiling increases, in which connection the content of each component passes a maximum. The data in Table 3 show that the reaction rate increases with increasing temperature. At 100 atm and 320 - 350°C a conversion of 60 - 80% is attained within 5 - 10 min. With rising temperature the content of low telomers decreases, that of higher telomers increases (Fig. 2). The experimental part describes the following reaction: 1) C_2H_4 with CH_3SiCl_2H . Methyl-ethyl-dichloro silane and methyl-n-butyl-dichloro silane were obtained. 2) C_2H_4 with $(C_6H_5)_3SiH$.

Triphenyl-ethyl-silane confirmed by infrared spectra and triphenyl-n-butyl-silane resulted, further a residue from $(C_6H_5)_3SiOSi(C_6H_5)_3$.

3) C_3H_6 with CH_3SiCl_2H in the presence of H_2PtCl_6 at room temperature.

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Thermal Telomerization of Olefins With
Silanes

S/062/60/000/04/03/006
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Result: $\text{CH}_3\text{SiCl}_2\text{n.C}_3\text{H}_7$ which was identified by means of its Raman spectrum. 4) Thermal telomerization of C_3H_6 with $\text{CH}_3\text{SiCl}_2\text{H}$ yielded $(\text{CH}_3)_3\text{Si-CH}_2\text{-CH}_2\text{-CH}_3$ (confirmed by Raman spectrum). These reactions did not obey the Markovnikov law. The infrared and Raman spectra were taken in the Institut organicheskoy khimii AN SSSR (Institute of Organic Chemistry of the AS USSR), for which the authors express their gratitude to L. A. Leytes. There are 2 figures, 3 tables, and 15 references: 13 Soviet, 1 British, 2 Japanese, and 2 American. X

ASSOCIATION: Institut elementoorganicheskikh sovedineniy Akademii nauk SSSR (Institute of Elemental-organic Compounds of the Academy of Sciences of the USSR)

SUBMITTED: July 23, 1958

Card 3/3

NESMEYANOV, A.M.; BORISOV, A.Ye.; NOVIKOVA, N.V.

Vinyl compounds of tri- and pentavalent antimony. Izv.AN SSSR
Otd.khim.nauk no.5:952 № '60. (MIRA 13:6)

1. Institut elementoorganicheskikh soedineniy Akademii nauk SSSR.
(Antimony compounds) (Vinyl compounds)

NESMEYANOV, A. N.

82101
S/062/60/000/07/04/007
B015/B054

5.3700

AUTHORS:

Nesmeyanov, A. N., Nogina, O. V., Berlin, A. M.,
Kudryavtsev, Yu. P.

TITLE:

Chemical Transformations of Dialkoxo Titanium Oxides ¹

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
1960, No. 7, pp. 1206-1214

TEXT: The authors describe the chemical properties of dialkoxo titanium oxides. They continued the investigation of deposition to the $\text{Ti} = \text{O}$ bond, studied the etherification reactions, and found the substitution of alkoxyls by halogens as well as a substitution reaction of the oxygen bound to titanium with two chlorine atoms. They obtained the first compounds of a hitherto unknown series of titanium-containing organic compounds, i.e., ethoxy-, n-propoxy-, and n-butoxy titanium oxide chlorides. By the action of chlorine on di-n-propoxy- and diisobutoxy titanium oxides, they produced the compounds $\text{Cl}_2\text{TiO} \cdot 2\text{n-C}_3\text{H}_7\text{OH}$ and $\text{Cl}_2\text{TiO} \cdot 2\text{i-C}_4\text{H}_9\text{OH}$. On the reaction of dialkyl dichloro silanes with dialkoxo titanium oxides, the following exchange of oxygen with two chlorine atoms takes place:

Card 1/2